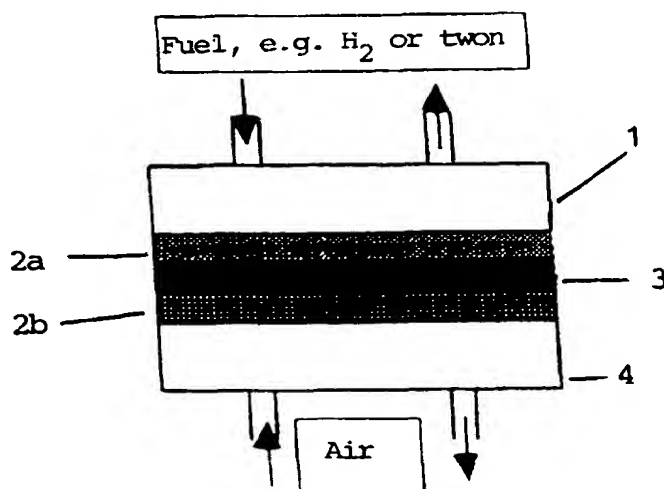


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE99/01046 <b>(22) International Filing Date:</b> 11 June 1999 (11.06.99) <b>(30) Priority Data:</b> 9802103-3      12 June 1998 (12.06.98)      SE <b>(71)(72) Applicant and Inventor:</b> ZHU, Bin [CN/SE]; KTH, Kemisk Teknologi, Teknikringen 42, S-100 44 Stockholm (SE). <b>(74) Agents:</b> BERG, S., A. et al.; Albihns Patentbyrå Stockholm AB, P.O. Box 5581, S-114 85 Stockholm (SE).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: A FUEL CELL



## (57) Abstract

A fuel cell for production of electrical energy, such as a fuel cell, comprising a fuel chamber (1), an anode (2a), a cathode (2b), an electrolyte (3) disposed between said anode and said cathode, an oxidant chamber (4), wherein said chambers (1 and 4) enclose said anode, cathode and electrolyte, wherein a fuel flowing from the fuel chamber is oxidised at the anode, thereby producing electrical energy, wherein said electrolyte (3) is a ceramic composite electrolyte comprising at least one salt and at least one oxide in mixture.

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## A fuel cell

### Field of the invention

This invention relates to a fuel cell and more particularly the invention relates to an intermediate temperature fuel cell.

The present invention is also relevant to catalysts and membrane reactors, such as hydrogen generator and penetration devices.

Furthermore, the invention is also relevant to devices for treatment of hazardous gases, such as desulphurisation, and waste chlorine treatment etc.

### Background of the invention

A fuel cell is an electrochemical cell which can continuously convert chemical energy of a fuel and an oxidant to electrical energy by a process involving an essentially invariant electrode-electrolyte system. Fuel cells work at high efficiency with emission levels far below the most strict standards. Fuel cell systems have the advantage of being modular, therefore they can be built in a wide range of power requirements, from a few hundred watts up to megawatts.

The basic principles of a fuel cell are those of well known electrochemical batteries. The difference is that in the case of batteries, the chemical energy is stored in substances located inside them. When this energy is converted to electrical energy, the battery must be thrown away (primary batteries) or recharged (secondary batteries).

In a fuel cell, the chemical energy is provided by a fuel and an oxidant stored outside the cell in which the chemical reactions take place.

The fuel cell comprises an anode, an electrolyte and a cathode. The fuel is oxidised at the anode, and the oxidant is reduced at the cathode. The reactions can be described as "cold combustion", giving water as combustion product. In between the anode/cathode is the electrolyte.

During the cold combustion in the fuel cell electrical work is produced corresponding to a change in free energy determined by the equation of Gibbs-Helmholtz (1) as follows:

5 
$$\Delta G = \Delta H - T \Delta S = U \cdot n \cdot F \quad (1)$$

10  $\Delta H$  being the change in enthalpy in J/mole when water is formed from its elements (corresponding to the amount of heat liberated at open combustion of hydrogen gas at constant pressure and temperature),  $T$  is the absolute temperature in K and  $\Delta S$  the change in entropy in J/K\*mole;  $U$  is the open voltage of the fuel cell,  $n$  is the number of electrons consumed at the reaction ( $n = 4$  for each water molecule formed for a hydrogen/oxygen cell) and  $F$  is Faraday's constant (96 485 As/mole).

15 The current density for fuel cell electrodes is limited by the reactants and normally reaches less than A/cm<sup>2</sup>.

For practical reasons, fuel cell systems are simply distinguished by the type of electrolyte used and the following names and abbreviations are now frequently used in literature: alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), solid/molten state cells (SSFC) such as: molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC) and proton exchange membrane fuel cells (PEMFC). The fuel cells mentioned above will be described in more detail below.

25 The alkaline fuel cell (AFC) is used for instance in the space and military industry, for instance in submarines.

Solid/molten state cells (SSFC) of today are of three basic types, PEMFC (Polymer electrolyte), MCFC (Molten Carbon) and SOFC (Solid Oxide).

Efforts have been made to construct solid state fuel cells using carbonate melts (MCFCs), but they usually have low efficiency.

PEMFCs use proton-exchange polymer membranes as electrolytes. The presence of water in the membranes limits the operational temperatures to below 100 °C. This causes slow electrode kinetics and low tolerance of electrodes to fuel impurities such as carbon monoxide (CO). As a result, neither hydrocarbons, nor hydrogen from hydrocarbon reforming (inevitably with CO) can be used as fuels for the PEMFCs. A further development thereof is polymer membranes, which can resist higher temperatures, such as 200 °C.

MCFCs use molten alkali carbonates retained in a matrix as the electrolyte. Such a device requires an operation temperature of about 650 °C to maintain a molten state with sufficient ionic conductivity. Although some MCFCs have been on the market, there are still several technological issues critically hindering the commercialisation progress, mainly concerning serious material corrosion problems.

SOFCs usually use ceramic membranes (YSZ). Limited by its ionic conductivity, the YSZs require an operational temperature of about 1000 °C, thereby resulting in considerable constraints on the materials used for interconnection, sealing and construction. However, as the electrolyte is solid—a mixture of yttria (Y<sub>2</sub>O<sub>3</sub>) and zirconia (ZrO<sub>2</sub>)—problems with liquid handling and corrosion are avoided. Charge transfer in the electrolyte is done by oxygen ions (O<sup>2-</sup>). Anodes made of nickel/zirconium oxide cermet were shown to be suitable; cathodes of lanthanum manganate (LaMnO<sub>3</sub>) have been used, but require still some additional research.

Electrode reactions are summarised for the proton conducting case as follows:

Anode reaction:  $\text{H}_2 (\text{g}) \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode reaction:  $2\text{H}^+ + 2\text{e}^- + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g/l})$

Overall reaction:  $\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g})$

As the cathodic reaction uses oxygen only (or air) as oxidant, recirculation of carbon dioxide from the anode exhaust is not necessary, and thereby simplifies the system considerably. Carbon monoxide does not poison the electrodes and can also be used as a fuel. Difficulties in the development of SOFCs arise from the instability of the intercell connections, i. e. the contact areas between the cells, and the sealing due to a high temperature (1000 °C). Also thermal cycling is a problem. This limits the application of these systems. Research on medium-temperature solid oxide fuel cells has been performed, in which the cells are hydrogen-oxygen cells, the solid material is hydrogen-exchanged  $\beta$ -alumina. The operating temperature for this type of solid proton conductor is 150-200 °C.

Internal fuel reforming is also possible. Sulphur is a big problem for all current fuel cell technologies, demanding an expensive gas treatment system, and also significantly decreasing the fuel cell system efficiency. Sulphate based electrolytes are chemically resistant to  $\text{H}_2\text{S}$  and any sulphur containing gases, such as natural gas. The use of  $\text{Li}_2\text{SO}_4$  as an electrolyte has been tested. This is described in D. Peterson and J. Winnick, J. Electrochem. Soc., 143 (1996) L55.

Catalysts have also been used to increase the output current of conventional fuel cells, which are batteries using galvanic cells powered by hydrogen and oxygen. Generally, such cells are fuelled by hydrogen gas derived from natural gas. There are also other techniques based on methanol, but they have not been successful.

Yet a new type of fuel cell was discovered in 1991, using a catalyst which gave a complete combustion of sugar, thereby forming carbon dioxide and water at a low temperature of just under 100 °C (Larsson Ragnar and Folkesson Börje, Lund University, Sweden.), the so-called "SuFuCell". This cell uses a bio fuel and saves global reserves of petroleum and natural gas. The carbon dioxide produced formed

in the cell is re-utilised in the photosynthesis to produce new sugar or starch. All kinds of carbon hydrates, such as starch, cellulose etc can be employed.

5 Although the prior art fuel cells using sugar offer many of above possibilities there is still a demand for a cell with better performance, which is also less expensive.

#### Summary of the disclosure

10 An object of the present invention, so called intermediate temperature ceramic fuel cells (ITCFCs), is to provide a fuel cell comprising a ceramic composite electrolyte, which fuel cell does not suffer from the drawbacks described above.

15 This is embodied in a ceramic membrane (CM) (electrolyte) and a ITCFC provided with such a membrane, according to the invention, which membrane (electrolyte) is based on salt-oxide ceramic composites.

According to a preferred embodiment of the invention, the ceramic membrane (electrolyte) is dense and gas tight.

20 According to another preferred embodiment of the invention the membrane (electrolyte) is oxygen ion conducting, for instance based on ceria based oxide composites, such as gadolinium doped ceria (CGO) and salt and possibly other inorganic compounds, to operate in ITSOFCs (300 to 800 °C) (Intermediate Temperature SOFCs).

25 According to another preferred embodiment of the invention, the membrane (electrolyte) is proton conducting ceramic composites based on halide- and hydrohalide-based ceramics, to operate in ITCFCs (Intermediate Temperature CFCs). Composite is referred to as a mixture with at least two different separated phases.

According to another preferred embodiment of the invention, there is provided a fuel cell, comprising

a fuel chamber

5 an anode,

a cathode,

an electrolyte disposed between the anode and cathode,

an oxidant chamber, wherein said chambers and enclose said anode, cathode and electrolyte,

10 wherein a fuel flowing from the fuel chamber, such as hydrogen is oxidised at the anode, thereby producing electrical energy, wherein said electrolyte is a ceramic composite electrolyte comprises at least one salt and at least one oxide.

In some extreme cases, the electrolyte can also have no oxide phase, being a two  
15 phase salt/inorganic compound, comprising at least one solid state phase, such as two fluoride phases, or one fluoride with one molten phase, MOH (M = Li, Na, K) etc.

Preferably, the electrodes, i. e. the anode and cathode, are porous.

20 The electrolyte can comprise up to 99 % salt and the salt can be in solid or molten state. Also in some cases, 100% salts with two phases, e.g., two fluorides (chlorides) or fluorides mixed with other pure salts, e.g.,  $MH_x$  (M = Li, Na, Ca etc.,  $x = 1, 2$ ) or  $MClx$  (M = Li, Na, Ba, Sr etc.,  $x = 1, 2$ ) are possible.

25 The salt (molten or solid state)-oxide composites (SOC) can be selected from all salts and oxides that can make the SOC material function as a specific conductor for particular ions such as  $H^+$ ,  $O^{2-}$ , or of other ionic charge, e.g., cationic  $Li^+$ ,  $Na^+$ ,  $K^+$ , or anionic,  $CO_3^{2-}$ ,  $Cl^-$  and  $F^-$  etc.), or a mixture thereof. Specific suitable salts and  
30 oxides can be such as various natural salts, NaCl etc., and oxides such as  $Al_2O_3$  etc., and synthesised compounds having similar properties.



Specific examples of SOCs comprise for instance: i) chlorite salts and composites which can have good  $\text{Cl}^-$  conduction. Therefore, the fuel cell according to the invention can also be used for treating industrial waste chlorine gas. ii) fluoride/hydrofluoride-based alumina composites can have excellent proton conduction. iii) Also in some cases, pure salt systems, e.g., two fluorides (chlorides) or fluorides mixed with other pure salts, e.g.,  $\text{MH}_x$  ( $\text{M} = \text{Li}, \text{Na}, \text{Ca}$  etc.,  $x = 1, 2$ ) or  $\text{MCl}_x$  ( $\text{M} = \text{Li}, \text{Na}, \text{Ba}, \text{Sr}$  etc.,  $x = 1, 2$ ) for proton conduction.

In some extreme cases, the electrolyte can comprise salt, say, two fluoride phases to 100%.

The oxide can be almost any suitable oxide, such as alumina, causing significant electronic and ion conduction. It is important that the material in the electrolyte is highly ion conducting.

The fuel employed can for instance be  $\text{H}_2$  or twon gas.

The intermediate temperature (300 - 800°C) allows use of cheap metals as electrode and interconnecting materials, which avoids high temperature (1000 °C) material and technical problems and also reduces the cost.

Furthermore, the fuel cell according to the invention can operate as a ceramic membrane electrochemical reactor. Fabrication techniques developed for inorganic membranes such as extrusion, tape casting and doctor-blade for porous ceramic support, tape casting, sol-gel/suspension, CVD techniques for both porous electrodes and dense electrolyte membranes, can also be readily employed in the fabrication.

For constructing high voltage devices, all current high performance oxide electrodes such as various binary oxides,  $\text{A}_x\text{B}_y\text{O}_z$  ( $\text{A}, \text{B} = \text{Li}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ,

Y, La, Ce, Zr, Ti, etc.), e.g.,  $\text{Ce}_{1-x}\text{BxO}_{2-y}$ ,  $\text{MnO}_2$  and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , and salt-oxide ceramic composite electrodes can be employed.

Since the device, in some cases, has the character of a combination of different galvanic cells, e.g., fuel cells and battery, a higher voltage than that of fuel cells can be achieved.

The device according to the present invention is as an ideal source for high power generation. One reason is because the materials comprised in the device are available in large amounts and highly cost effective. In addition, there is no need for expensive catalysts as in conventional low temperature fuel cells, i. e., operating below  $200^\circ\text{C}$ . The device according to the invention can function at intermediate temperatures, say,  $300$  to  $800^\circ\text{C}$ .

The results obtained from the fluoride-based ceramic composite electrolyte fuel cells show a short circuit current density close to  $1000\text{ mA/cm}^2$  and peak power of  $180\text{ mW/cm}^2$ , which is below  $300\text{ mA/cm}^2$  ( $0.6\text{ V}$ ), at  $750^\circ\text{C}$ , see Fig. 1. However, there is a large potential for further development, since the results are obtained for bulk and raw disk-type electrolytes only. It can be expected that performance will be significantly improved by a person skilled in the art, by using this technology. The key issue is to optimise electrolyte by employing ceramic membrane technologies, and develop more efficient and compatible electrodes for the new CFCs, which are also claimed.

#### Brief description of the drawings

The present invention will now be described in more detail with reference to preferred embodiments of the invention, given only by way of example, and illustrated in the accompanying drawings, in which:

Fig. 1 illustrates a fuel cell according to the invention;

Fig. 2 illustrates time dependence of an open circuit voltage (OCV) at 450 °C according to one embodiment of the invention;

Fig. 3 illustrates temperature dependence of the OCV according to one embodiment of the invention;

Fig. 4 illustrates a typical current-voltage (I-V) characteristic of a fuel cell device using commercial NaCl salt as one of the main components of the electrolyte.

Fig. 5 illustrates a typical I-V characteristic of a fuel cell device using the hydro-fluoride-based composite electrolyte.

Fig. 6 illustrates discharge curves for the fuel cell illustrated in Fig. 5 during operation with various current outputs.

#### Detailed description of the preferred embodiments

Referring to Fig. 1, the fuel cell 1 according to invention essentially consists of two porous electrodes 2 separated by a dense, proton (or oxygen) conducting salt-oxide (or composite) electrolyte 3, where anode 2a and cathode electrodes 2b can be made of e.g., spinel or perovskite oxides, and the fuel and oxidant chambers 4 surrounding said electrodes 2 can be made of a metal, such as stainless steel.

The fuel circulates in the fuel chamber and part of the fuel is oxidised at the anode. At the same time air is oxidised at the cathode.

Because of the electrochemical cell reaction:  $\text{H}_2 + 1/2 \text{O}_2 = \text{H}_2\text{O}$  at the cathode side, the formation of the cell reaction product,  $\text{H}_2\text{O}$  can be exhausted together with the air (oxygen), so that the fuel can be re-cycled without requiring water elimination. Thus, it is easy to simplify the device, reduce the fuel cost and also increase the efficiency of the fuel-energy conversion.

The free energy change of the combustion of the device in Fig. 1 corresponds to an open cell voltage (OCV) of 1.23 V at ambient temperature (25 °C). For high temperatures, this OCV value follows a linear decreasing curve, between 1.0 to 1.2 V. The device can reach a voltage of up to 1.8 V, which is only achieved for limited electrode pair materials. Such a high cell voltage is assumed to be caused by a combination of battery and fuel cell effects.

#### Current Output and Operating Efficiency

In Fig. 5. A current output of 300 mA/cm<sup>2</sup> at a cell voltage 0.6 V at 740 °C, corresponded to a power of 180 mW/cm<sup>2</sup>. The cell voltage operating electricity efficiency is  $0.6/1.2 = 50\%$ . This efficiency can be further increased by the electrolyte conductivity and compatible electrode materials. Most power loss during operation is recognised due to the interfacial loss, since the oxide electrodes are not excellently compatible with the salt electrolytes.

#### Voltage

Voltages depended on both electrolytes and electrodes. An example of the unusual high voltage device is constructed as:

Doped NiOx /salt-oxide ceramic composites/LaSrCoFeO.

#### Materials

Composites of salts, specially, chlorides, fluorides and hydro-type-halides containing MH<sub>x</sub> etc., and oxides have been successfully synthesised for electrolyte materials, and some of them used also as electrode materials, for intermediate temperature, say 300 to 800°C, fuel cell (ITFC) devices. The materials can use natural resources and synthesising technique has a great flexibility in selection of materials, and advantages of easy preparation, large scale products available and high cost effective.

It is possible to use synthesised salt-alumina composite containing min. 99.9% salt, e.g., NaCl as main components to prepare proton conducting salt-oxide composite ceramics. A fuel cell device using  $MCl_x$ - based composite electrolyte has achieved 1.0 to 1.4 V cell voltage between 350 to 700°C, and several hundreds of mA/cm<sup>2</sup> can be drawn from this fuel cell.

Due to an excellent chemical stability of sulphate-based electrolytes with H<sub>2</sub>S, the fuel cell can use H<sub>2</sub>S as fuel, which may work as a desulphonication device for sulphur recovery and treatment of hazardous gases. The device can be continuously operated with stable current output. During the operation, sulphur and water were collected from the anode and cathode, respectively, indicating success in H<sub>2</sub>S removal and electricity generation. Thus, it is possible to use natural gas, coal and other sulphur containing gas as fuels without a high extra cost compared to a traditional clean-up station, due to the extra electricity production.

CFCs using the fluoride based electrolytes have may use various liquid fuels for operation. The direct use of logistic fuels such as ethanol or kerosene will simplify the introduction of the fuel cell technology into the commercial market. It is possible to use ethanol or even gasoline as fuel.

The ITCFCs show unique advantages for operating liquid fuels due to high proton conduction and fast electrode kinetics in the intermediate temperature region, without use of noble catalysts. A direct ethanol CFC device has been operated up to 200 mAcm<sup>-2</sup> at 700 °C.

Some more examples are merely intended to illustrate the invention, and are not limiting.

### Examples

Unusual examples

Example 1

In ambient atmosphere, the device according to the invention, illustrated in Fig. 1 showed an OCV between 0.4 to 0.6 V, for both electrodes, whereby the current that could be drawn out rapidly decreased. As long as hydrogen was supplied to the anode of doped NiOx, and air to the cathode of LaSrCoFeO, the OCV suddenly jumped to about 1.0 V, and increased with time gradually to about 1.5 to 1.8 V. When the hydrogen supply was removed, the OCV first dropped steeply then decreased gradually with time. These observations are schematically shown in Fig. 2. Further tests were done by exchanging the electrode sides, i.e., the hydrogen was supplied to the LaSrCoFeO electrode, and air to the doped NiOx electrode, whereby the device showed an OCV close to the former OCV value but with negative sign.

Fig. 3 shows two curves for devices according to the invention using different salt electrolytes. Several tens to hundred of mA/cm<sup>2</sup> can be taken out from the devices. A typical current density-voltage curve (I-V curve) is shown in Fig. 4.

Example 2 (non electrode construction)

When using only electrolyte GdxCe1-x pellet to achieve fuel cell devices without electrodes, an OCV of such a "non-electrode construction" fuel cell device is 0.96 V, i. e., about 0.2 V higher than conventional constructions with electrode using the same electrolyte. Only about 2 mA/cm<sup>2</sup> can be taken out from this device. The function is based on the fact of the ionic conducting bulk material, GdxCe1-x as the electrolyte, on each of its surface, whereby the significant electronic and ionic conduction can be caused when reacting with the gas and function as anode and cathode, respectively. It is discovered that the performance of this device was recognised to be limited by the air surface, because in the air (or oxygen) the GdxCe1-x does not create enough electronic conduction, resulting in that an improved construction was made using only one electrode, of e.g., Pt or Ag (paste) for the cathode, i.e.,

(H<sub>2</sub>)GdxCe1-x /Pt or Ag (air)

In this device, the current can be increased by almost one order of magnitude. The further improvement can be done regarding the ion-doping technique to prepare sufficient electronic conducting ceria-based materials. It can be seen clearly from this fuel cell device without using electrode materials, that the SOFC technology will be greatly simplified and more cost effective. Using doped  $\text{Bi}_2\text{O}_3$ -based oxides instead of doped ceria-based oxide electrolytes will improve cell performance to a large extent.

### Example 3 (practical devices)

Fuel cells using the fluoride and hydrofluoride-based composite electrolytes (proton conducting type) and ceria-salt (halides) composite electrolytes are typical examples for practical ITCFC devices, one example is shown in Fig. 5. All these new type ITCFCs have demonstrated a performance well reach the present commercialising standards. In addition, ITCFCs using the sulphate-based electrolytes as the high sulphur tolerant device can treat high sulphur containing fuels, e.g., natural gas or by-products from the refining petroleum process, and at the same time to produce the electricity. This sulphur tolerant CFC device can be expected as the gas-pre-treatment station combined with MCFC power plant to invent a new power generation technology.

It will be appreciated by those skilled in the art that the examples mentioned above are primarily for the purpose of illustration and are not meant to imply any limitation of the present invention.

## Claims

1. A fuel cell for production of electrical energy, comprising

5 a fuel chamber (1)

an anode (2a),

a cathode (2b),

an electrolyte (3) disposed between said anode and said cathode,

10 an oxidant chamber (4), wherein said chambers (1) and (4) enclose said anode, cathode and electrolyte,

wherein a fuel flowing from the fuel chamber is oxidised at the anode, thereby producing electrical energy,

characterised in that:

15

said electrolyte (3) is a ceramic composite electrolyte comprising at least one salt, and at least one oxide in mixture.

20 2. A fuel cell according to claim 1, wherein the electrolyte can comprise up to 99 % salt.

3. A fuel cell according to claim 1 or 2, wherein the oxide in the electrolyte can be any suitable oxide, such as alumina, or  $\text{SiO}_2$  etc.

25 4. A fuel cell according to any one of the claims 1-3, wherein the electrolyte comprises salts selected from all salts that can make the SOC material function as a specific conductor for particular ions such as  $\text{H}^+$ ,  $\text{O}^{2-}$ , or of other ionic charge, e.g., cationic  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , or anionic,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{F}^-$  etc.), or a mixture thereof, preferably cheap salts can be used such as various natural salts, e.g.,  $\text{NaCl}$ , and synthesised compounds having similar properties.

30



5. A fuel cell according to claim 1 or 2, wherein the electrolyte comprise ceria-based oxide-salt compounds, e.g., GCO-MCl<sub>x</sub>, containing salt from 1 - 50%.

5 6. A fuel cell according to any one of the claims 1-4, wherein the electrodes comprises binary oxides, such as A<sub>x</sub>B<sub>y</sub>O<sub>z</sub> (A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr, Ti, etc.), typically, LiMO<sub>2</sub> (M = Ni, Co, Mn), Ce<sub>1-x</sub>B<sub>x</sub>O<sub>2-y</sub>, MnO<sub>2</sub> and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>.

10 7. A fuel cell according to claim 1 or 2, wherein the electrolyte comprises halid and hydro-halide-based composite.

15 8. A fuel cell according to claim 1 or 2, wherein the electrolyte is sulphate-based for sulphur containing fuels, intended to operate as a high sulphate tolerant CFC device, acting as a pre-gas treatment station and intended to be combined with MCFC power plants.

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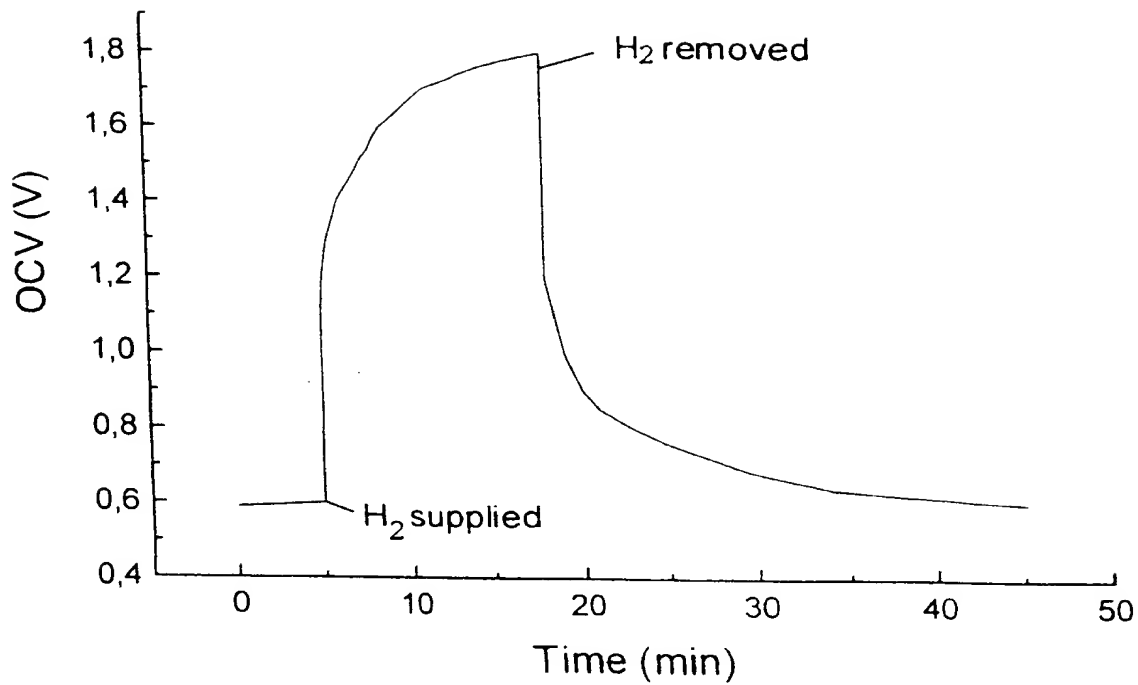


FIG. 2

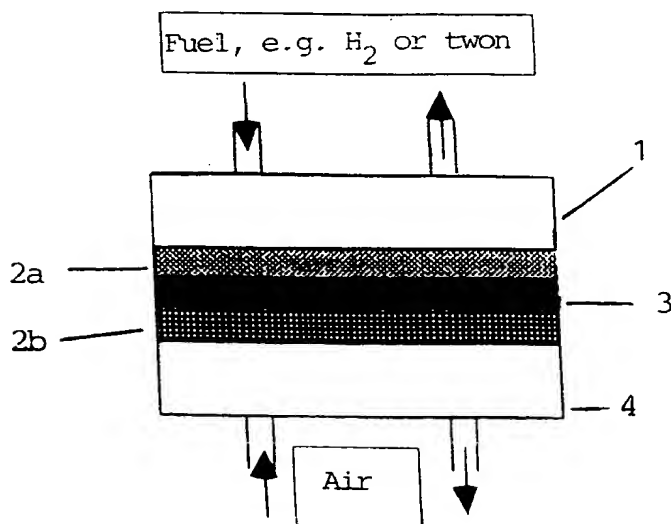


FIG. 1

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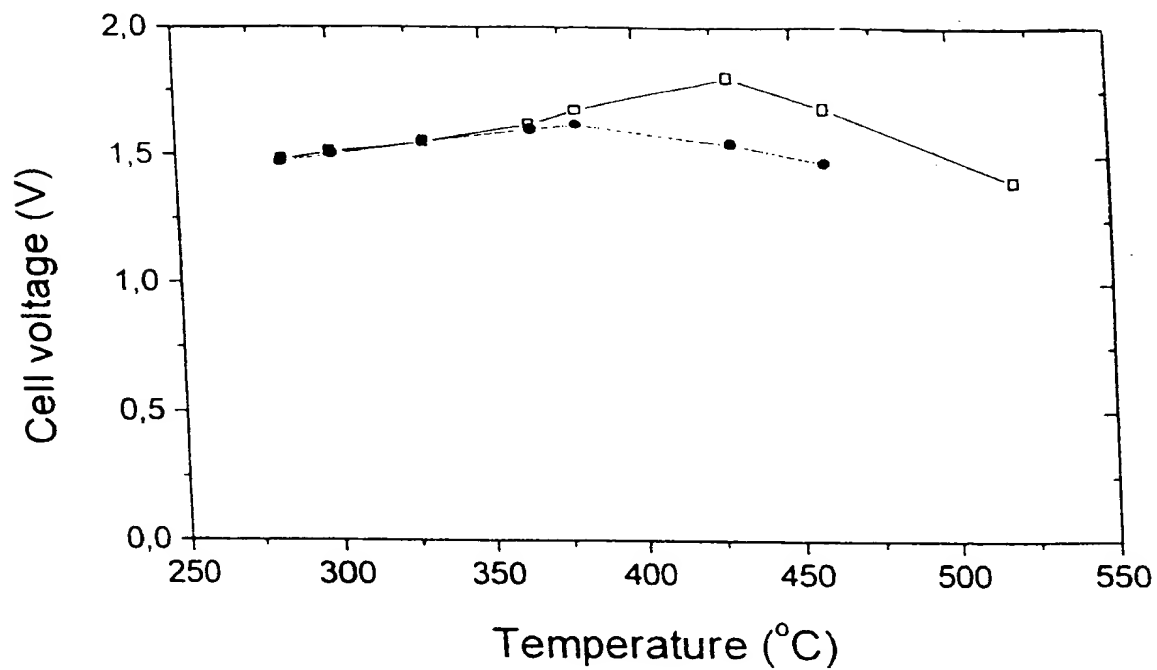


FIG. 3

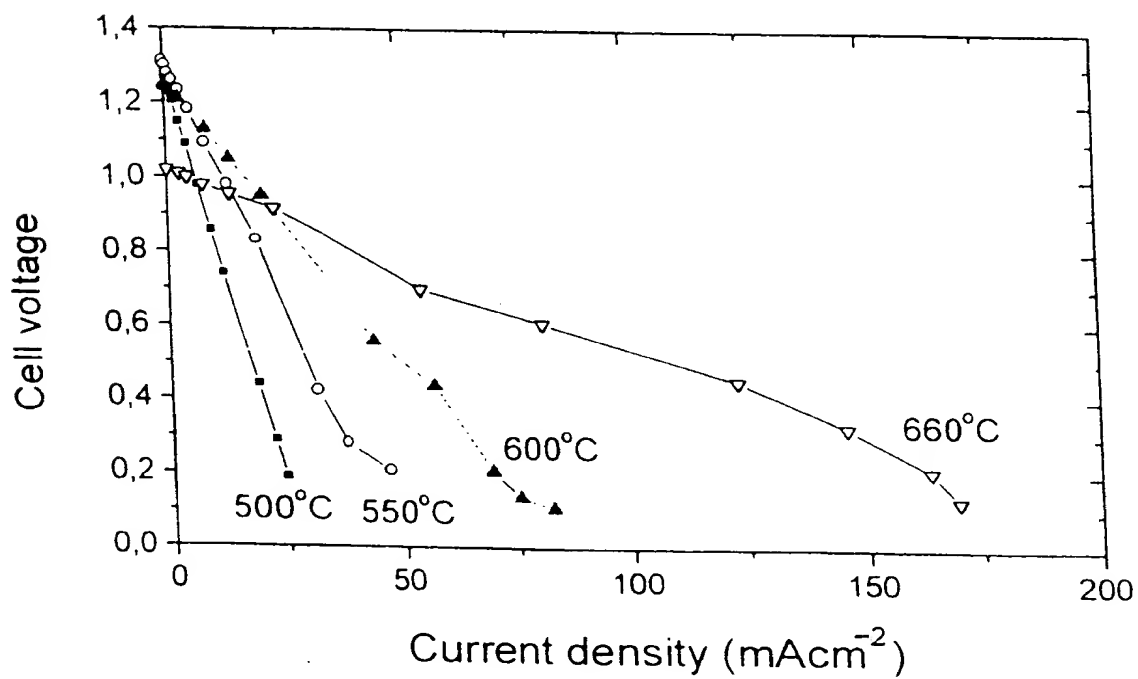


FIG. 4

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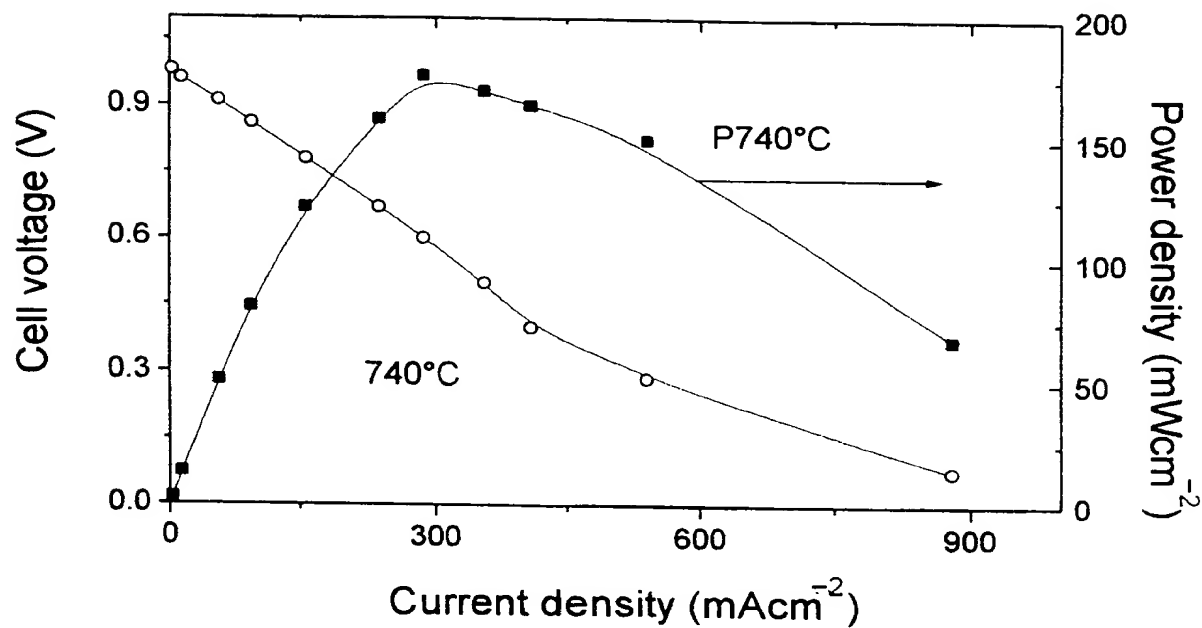


FIG. 5

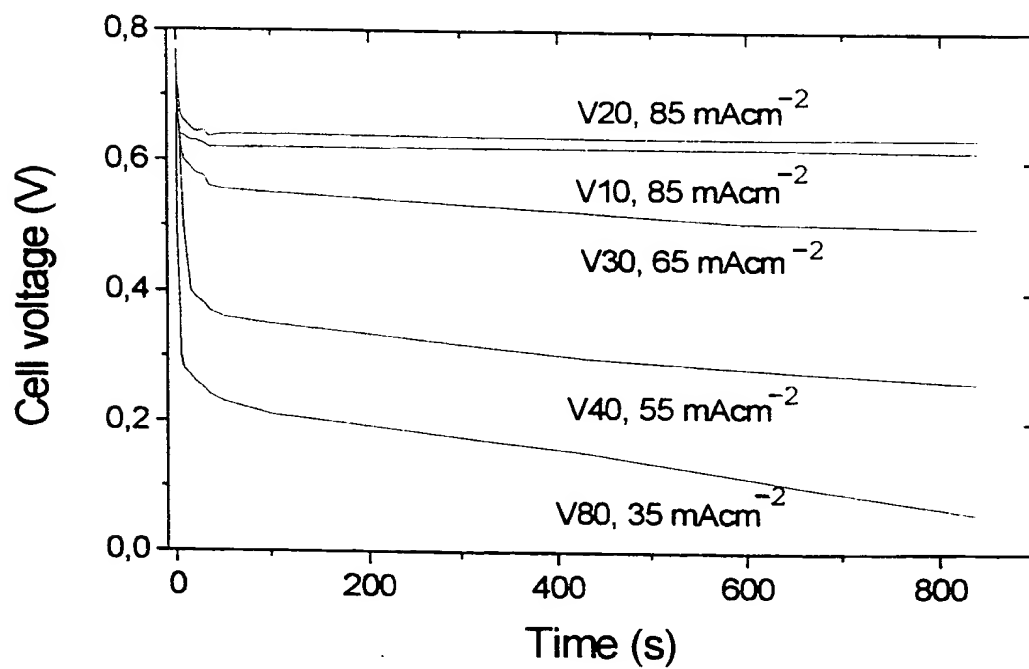


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01046

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 8/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 60074270 A (ASAHI GLASS CO LTD) 1985-04-26 (abstract) World Patetns Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 1999-10-18). Retrieved from: EPO WPI Database. DW198523, Accession No. 1985-138099; & JP 60074270 (ASAHI GLASS CO LTD) 1985-08-29 (abstract). (online)(retrieved on 1999-10-18). Retrieved from: EPO PAJ Database --	1,3,6,7
X	US 3497389 A (C. BERGER ET AL), 24 February 1970 (24.02.70), column 2, line 23 - line 72; column 3, line 12 - line 36; column 6, line 17 - line 75 --	1
A	US 3351491 A (BRYAN SIDNEY HARRIS ET AL), 7 November 1967 (07.11.67), column 2, line 5 --	1-8

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

18 October 1999

Date of mailing of the international search report

03 November 1999 (03.11.99)

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Ulla Granlund/ELY

Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01046

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5632874 A (NIELS CHRISTIANSEN), 27 May 1997 (27.05.97), column 1, line 48 - column 2, line 13  -- -----	1-8

### Information on patent family members

International application No.

PCT/SE 99/01046

Form PCT/ISA/210 (patent family annex) (July 1992)

WO 99/65098

PCT/SE99/01046

14

REPLACED BY  
ART 34 AMDT**Claims**

1. A fuel cell for production of electrical energy, comprising
- 5 a fuel chamber (1)  
an anode (2a),  
a cathode (2b),  
an electrolyte (3) disposed between said anode and said cathode,  
an oxidant chamber (4), wherein said chambers (1) and (4) enclose said anode,  
10 cathode and electrolyte,  
wherein a fuel flowing from the fuel chamber is oxidised at the anode, thereby producing electrical energy,
- characterised in that:
- 15 said electrolyte (3) is a ceramic composite electrolyte comprising at least one salt, and at least one oxide in mixture.
2. A fuel cell according to claim 1, wherein the electrolyte can comprise up to 99 %  
20 salt.
3. A fuel cell according to claim 1 or 2, wherein the oxide in the electrolyte can be any suitable oxide, such as alumina, or  $\text{SiO}_2$  etc.
- 25 4. A fuel cell according to any one of the claims 1-3, wherein the electrolyte comprises salts selected from all salts that can make the SOC material function as a specific conductor for particular ions such as  $\text{H}^+$ ,  $\text{O}^{2-}$ , or of other ionic charge, e.g., cationic  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , or anionic,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{F}^-$  etc.), or a mixture thereof, preferably cheap salts can be used such as various natural salts, e.g.,  $\text{NaCl}$ , and synthesised compounds having similar properties.
- 30



WO 99/65098

PCT/SE99/01046

15

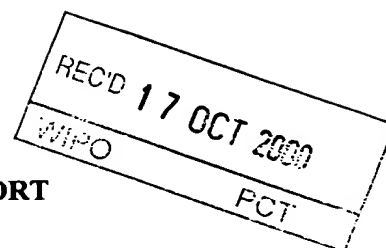
5. A fuel cell according to claim 1 or 2, wherein the electrolyte comprise ceria-based oxide-salt compounds, e.g.,  $GCO-MCl_x$ , containing salt from 1 - 50%.
- 5 6. A fuel cell according to any one of the claims 1-4, wherein the electrodes comprises binary oxides, such as  $A_xB_yO_z$  (A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr, Ti, etc.), typically,  $LiMO_2$  (M = Ni, Co, Mn),  $Ce_{1-x}B_xO_{2-y}$ ,  $MnO_2$  and  $La_{1-x}Sr_xMnO_3$ .
- 10 7. A fuel cell according to claim 1 or 2, wherein the electrolyte comprises halid and hydro-halide-based composite.
- 15 8. A fuel cell according to claim 1 or 2, wherein the electrolyte is sulphate-based for sulphur containing fuels, intended to operate as a high sulphate tolerant CFC device, acting as a pre-gas treatment station and intended to be combined with MCFC power plants.

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



15

Applicant's or agent's file reference 51017-55888	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/SE99/01046	International filing date (day/month/year) 11.06.1999	Priority date (day/month/year) 12.06.1998
International Patent Classification (IPC) or national classification and IPC <sub>7</sub> H 01 M 8/10		
Applicant Zhu, Bin		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 12.01.2000	Date of completion of this report 12.10.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Ulla Granlund/ELY Telephone No. 08-782 25 00

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01046

## I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

☐ the international application as originally filed.

☒ the description, pages 1-12, as originally filed,  
pages \_\_\_\_\_, filed with the demand,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☒ the claims, Nos. \_\_\_\_\_, as originally filed,  
Nos. \_\_\_\_\_, as amended under Article 19,  
Nos. \_\_\_\_\_, filed with the demand,  
Nos. 1-4, filed with the letter of 10.10.2000,  
Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☒ the drawings, sheets/fig 1-6, as originally filed,  
sheets/fig \_\_\_\_\_, filed with the demand  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

2. The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_

☐ the claims, Nos. \_\_\_\_\_

☐ the drawings, sheets/fig \_\_\_\_\_

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01046

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	<u>1-4</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-4</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-4</u>	YES
	Claims		NO

**2. Citations and explanations**

The claimed invention according to amended claims of 10-10-2000 relates to a fuel cell and is intended to solve problems regarding the performance of the cell.

The solution of the problem according to the invention comprises a ceramic composite electrolyte comprising at least one salt and at least one oxide in mixture.

The documents cited in the international search report, JP 60074270 and US A 3497 389, are not considered to be of particular relevance to the amended claims.

JP 60074270 discloses a fuel cell with a ceramic electrolyte comprising an oxide and a salt in mixture. The oxide is  $ZrO_2$ , the salt is a fluoride and the electrodes comprise binary oxides.

US A 3497389 (column 2 line 23-72, column 3 line 12-36, column 6 line 17-75, claim 11) discloses a fuel cell with a ceramic electrolyte membran comprising an oxide and a salt in mixture. The mixture is pressed and then sintered. The electrolyte can comprise up to 80% of a salt such as calcium chloride.

The invention differs from each of the cited documents in the respect that the electrolyte is a ceramic ceria salt composite comprising at least one salt and at least one ceria phase.

Therefore, the claimed invention as stated in claims 1-4 is novel. It is further considered to involve an inventive step as the ceramic ceria salt composite electrolyte enables a fuel cell with high performance. It is also considered to be industrially applicable.

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 51017-55888	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/SE99/01046	International filing date (day/month/year) 11.06.1999	Priority date (day/month/year) 12.06.1998
International Patent Classification (IPC) or national classification and IPC H 01 M 8/10		
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- II ☐ Priority
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- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 12.01.2000	Date of completion of this report 12.10.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Ulla Granlund/ELY Telephone No. 08-782 25 00

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01046

## I. Basis of the report

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☐ the international application as originally filed.

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pages \_\_\_\_\_, filed with the demand,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☒ the claims, Nos. \_\_\_\_\_, as originally filed,  
Nos. \_\_\_\_\_, as amended under Article 19,  
Nos. \_\_\_\_\_, filed with the demand,  
Nos. 1-4, filed with the letter of 10.10.2000,  
Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

☒ the drawings, sheets/fig 1-6, as originally filed,  
sheets/fig \_\_\_\_\_, filed with the demand  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

## 2. The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_

☐ the claims, Nos. \_\_\_\_\_

☐ the drawings, sheets/fig \_\_\_\_\_

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01046

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. Statement

Novelty (N)	Claims	<u>1-4</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-4</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-4</u>	YES
	Claims		NO

## 2. Citations and explanations

The claimed invention according to amended claims of 10-10-2000 relates to a fuel cell and is intended to solve problems regarding the performance of the cell.

The solution of the problem according to the invention comprises a ceramic composite electrolyte comprising at least one salt and at least one oxide in mixture.

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JP 60074270 discloses a fuel cell with a ceramic electrolyte comprising an oxide and a salt in mixture. The oxide is  $ZrO_2$ , the salt is a fluoride and the electrodes comprise binary oxides.

US A 3497389 (column 2 line 23-72, column 3 line 12-36, column 6 line 17-75, claim 11) discloses a fuel cell with a ceramic electrolyte membran comprising an oxide and a salt in mixture. The mixture is pressed and then sintered. The electrolyte can comprise up to 80% of a salt such as calcium chloride.

The invention differs from each of the cited documents in the respect that the electrolyte is a ceramic ceria salt composite comprising at least one salt and at least one ceria phase.

Therefore, the claimed invention as stated in claims 1-4 is novel. It is further considered to involve an inventive step as the ceramic ceria salt composite electrolyte enables a fuel cell with high performance. It is also considered to be industrially applicable.

The Swedish Patent Office  
PCT International Application

14

PCT/SE99/01046

10 October 2000

## Claims

1. A fuel cell for production of electrical energy, comprising  
a fuel chamber (1)
- 5 an anode (2a),  
a cathode (2b),  
an electrolyte (3) disposed between said anode and said cathode,  
an oxidant chamber (4), wherein said chambers (1) and (4) enclose said anode, cathode  
and electrolyte,
- 10 characterised in that:  
said electrolyte (3) is a ceramic CSC (ceria salt composite) electrolyte comprising at  
least one salt and at least one ceria phase.
2. A fuel cell according to claim 1, wherein the electrolyte comprises salts selected  
15 from salts that can make the CSC material function as a specific conductor for  
particular ions such as  $H^+$ ,  $O^{2-}$ , or of other ionic charge, e.g., cationic  $Li^+$ ,  $Na^+$ ,  $K^+$ , or  
anionic,  $CO_3^{2-}$ ,  $Cl^-$  and  $F^-$  etc., or a mixture thereof, preferably natural salts, e.g. NaCl.
3. A fuel cell according to claim 1 or 2, wherein the electrodes comprises binary  
20 oxides, such as  $A_xB_yO_z$  ( $A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr,$   
 $Ti$ , etc.), typically,  $Li_xMO_y$  ( $M = Ni, Co, Mn$ ),  $Ce_{1-x}B_xO_{2-y}$ ,  $MnO_2$  and  
 $La_{1-x}Sr_xMn(Co)O_3$ .
4. A fuel cell according to claim 1, wherein the electrolyte is sulphate-based CSC for  
25 sulphur containing fuels, intended to operate as a high sulphur tolerant CFC device,  
acting as a pre-gas treatment station and intended to be combined with MCFC power  
plants.



## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing</b> (day/month/year) 16 March 2000 (16.03.00)	
<b>International application No.</b> PCT/SE99/01046	<b>Applicant's or agent's file reference</b> 51017-55888
<b>International filing date</b> (day/month/year) 11 June 1999 (11.06.99)	<b>Priority date</b> (day/month/year) 12 June 1998 (12.06.98)
<b>Applicant</b> ZHU, Bin	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
12 January 2000 (12.01.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b> R. E. Stoffel Telephone No.: (41-22) 338.83.38
--	--

1

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01046

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 8/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 60074270 A (ASAHI GLASS CO LTD) 1985-04-26 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 1999-10-18). Retrieved from: EPO WPI Database: DW198523, Accession No. 1985-138099; & JP 60074270 (ASAHI GLASS CO LTD) 1985-08-29 (abstract). (online)(retrieved on 1999-10-18). Retrieved from: EPO PAJ Database	1,3,6,7
X	US 3497389 A (C. BERGER ET AL), 24 February 1970 (24.02.70), column 2, line 23 - line 72; column 3, line 12 - line 36; column 6, line 17 - line 75	1
A	US 3351491 A (BRYAN SIDNEY HARRIS ET AL), 7 November 1967 (07.11.67), column 2, line 5	1-8

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited document:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

18 October 1999

Date of mailing of the international search report

03 November 1999 (03.11.99)

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Ulla Granlund/ELY

Telephone No. +46 8 782 25 00

2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01046

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5632874 A (NIELS CHRISTIANSEN), 27 May. 1997 (27.05.97), column 1, line 48 - column 2, line 13  -----	1-8

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/09/99

International application No.

PCT/SE 99/01046

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	3497389	A	24/02/70	DE	1442399 A	21/11/68
				GB	1126047 A	00/00/00
				SE	317646 B	24/11/69
US	3351491	A	07/11/67	DE	1496180 A	03/04/69
				GB	1032353 A	00/00/00
US	5632874	A	27/05/97	AU	688069 B	05/03/98
				AU	2854995 A	29/02/96
				CA	2152651 A	18/02/96
				DK	95394 A	18/02/96
				DK	171537 B	23/12/96
				EP	0697594 A	21/02/96
				JP	8206476 A	13/08/96
				NO	953222 A	19/02/96
				ZA	9506839 A	28/03/96